Senior Thesis

A look at Selenium as a trace element contaminant, and its relationship to sulfur, in the Kesterson National Wildlife Refuge, California.

by
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ABSTRACT

Selenium is a trace element that has warranted considerable attention within the past decade. Selenium is a member of the sulfur family and resembles sulfur both in its various forms and in its compounds. In this research, a case study was analyzed for the toxic levels of selenium in the Kesterson National Wildlife Refuge. Several factors as to why and how selenium accumulated in the refuge are discussed. Also, there is a brief analysis of sulfur and tellurium in relation to selenium and their potential toxicities. Samples collected from the Kesterson National Wildlife Refuge were also analyzed and discussed. A Graphical representation is made to show the enrichment of most environmental systems with selenium, sulfur and tellurium. These graphs were to express a consistent fractionation of sulfur to selenium, but was not conclusive to due insufficient studies in their chemical contaminant relationships. There are very similar chemical and geochemical processes that liberate the toxic compounds of selenium and sulfur and both of these elements could become potentially lethal problems if ignored.

TABLE OF FIGURES, TABLES, AND MAPS

Introduction

Most people in the United States upon hearing of trace element contamination think of elements like lead, mercury and cadmium. Selenium may soon be listed among one of the potentially harmful toxic trace elemental substances also. In **Section** I of this paper, the element selenium is discussed. Elemental selenium and its compounds, through geological, chemical and physical means can become incorporated into different environmental systems and cause harmful effects in high levels. In **Section** II, a case study of selenium contamination is discussed. The Kesterson National Wildlife Refuge and Reservoir was the terminus for agricultural drainage and runoff from some 77,000 acres of the San Joąquin Valley, diverted by the unfinished San Luis Drain, to undergo natural biofiltering and settling. But before the drain was to be completed, an environmental assessment was needed for approval. Through this assessment, the contamination of the ecological system, by high levels of selenium, was discovered. This well documented case has proved to be one of the most serious cases known in the United States. The selenium was concentrated through continuous draining of the agricultural effluents through naturally high seleniferous soils and sediments into the series of ponds and the reservoir at the refuge. The selenium bioaccumulated and became toxic within the ecological system through various means and in various forms. Selenium toxicity is then discussed in **Section** III. The refuge and reservoir were eventually closed in 1986 and

remediation was undertaken to rectify the problem of the high concentrations of selenium.

Because selenium is a member of the sulfur family, and chemically is very similar, it is my concern that perhaps the levels of sulfur and possibly tellurium in the Kesterson were high also, contributing to the potential problems that could be associated with selenium contamination and toxicity. In **Section IV**, the chemistry of sulfur and its potential toxicity are discussed. Tellurium is briefly discussed also due to its very similar chemical properties to selenium.

In 1993, I collected water and biological samples from points in the vicinity of the Kesterson National Wildlife Refuge. These samples were then analyzed for their concentrations of sulfur and selenium using the Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The collection and methods used for this analysis are discussed in **Section V**. The concentrations of selenium and sulfur were measured on the ICP-MS and then plotted on a composite graph compiled from reported literature values for sulfur and selenium concentrations in various materials. The standard reference line for the fractionation of sulfur to selenium was determined from the chondrite values from the data of Anders and Ebihara, 1982. This reference line was chosen because it was the most recent determination that was most representative of the natural abundance. The deviation from this line could then be correlated to the enrichment or depletion of either of these elements in other materials. The concentrations

of sulfur or selenium that produces harmful effects to environmental species or humans can also be shown from this graph. These graphical representations are discussed in **Section VI**. The very last section, **Section VII**, provides my conclusions.

SECTION I. SELENIUM

General Chemistry of Selenium

Selenium (chemical symbol of Se) has an atomic weight of 78.96 grams per mole and an atomic number of 34. It was discovered by Berzelius in 1817, who found it from sulfur used in the Swedish sulfuric acid industry. The element is a member of the sulfur family and resembles sulfur both in its various forms and in its compounds. See Figure 1 for selenium's location on the periodic table of the elements.

FIGURE 1. Geochemical classification of the elements in the periodic table. The classification is based on the way the elements distribute themselves between an iron liquid (siderophile), a sulfide liquid (chalcophile), a silicate liquid (lithophile), and a gas phase (atmophile). From Faure, G.,1991. Principles and Applications of Inorganic Geochemistry. Macmillan Publishing Company, pp. 95.

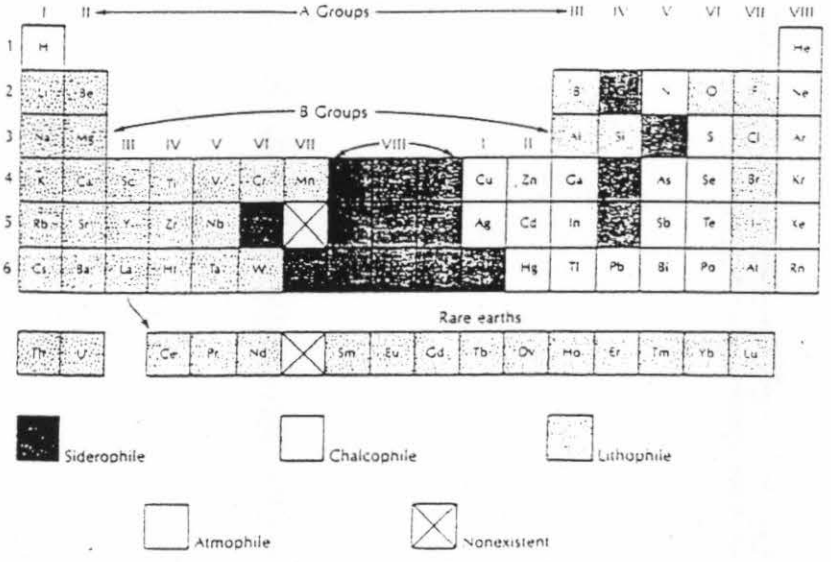


Figure 1.

The nonmetallic element is found in four primary forms in the environment. Selenium exists in several allotropic forms [41]. Three are generally recognized, but as many as six have been claimed. In anion form, selenide, with an oxidation state of -2, is usually associated with sulfide or minerals, such as pyrite, chalcopyrite, and bornite. Elemental selenium, the pure element, is concentrated usually with metals like copper or sulfur in three forms: 1) amorphous selenium is either red, in powder form, or black, in vitreous form, 2) crystalline monoclinic selenium is a deep red; crystalline hexagonal selenium (red and gray), or 3) insoluble, the most stable variety, is a metallic gray. In cation form, selenite (IV) is highly toxic when soluble but is normally bound tightly to iron, aluminum, or other metals and hence is not available as an active toxic compound. Selenate (VI), which is very soluble and highly toxic, is easily leached from the soil in this form in an alkaline environment, and is readily taken up by roots of many plants. Selenium also occurs in some rare minerals like berzelianite (Cu_2Se), tiemarrnite (HgSe), naumannite (Ag_2Se), eucairite (CuAgSe), zorgite (PbCuSe), and crookesite $(CuTlAg)_2Se$. Other minerals containing selenium are listed on Table 1. Natural selenium contains six stable isotopes. Fifteen other isotopes have been characterized. In years past it has been obtained from flue dusts remaining from processing copper sulfide ores, but the anode muds from electrolytic copper refineries now provide the source of most of the world's selenium. Selenium is recovered by

TABLE 1. Selenium Bearing Minerals

Cation	Name	Formula	Synonyms	Reference
		I. Native elements and Intermetallic Compounds		
	Native selenium	Se		
	Tellurium selenide	TeSe		
		II. Selenides		
	Hydrogen selenide	H_2Se		
Ag	Naumannite	Ag_2Se	Cacheutaite	
	Aguilarite	Ag_4SeS		
Ag–Bi	Bohdanowiczite	$AgBiSe_2$		5
Ag–Cu	Eucairite	AgCuSe		
Ag–Cu–Tl	Crookesite	$(Cu,Tl,Ag)_2Se$		
Pb	Clausthalite	PbSe	Lead Selenide	
Zn	Stilleite	ZnSe(?)		
Cd	Cadmoselite	CdSe		
Hg	Tiemannite	HgSe		
	Onofrite	Hg(S,Se)		
Fe	Achavalite	FeSe		
	Ferroselite	$FeSe_2$		
Cu	Klockmannite	CuSe		
	Berzelianite	Cu_2Se	Selenocuprite, copper selenide, berzeline	
	Umangite	$Cu_{4-x}Se_2$		
Cu–Fe	Eskebornite	$CuFeSe_2$		31
Ni	Blockite	$NiSe_2$	Penroseite	
	Wilkmanite	Ni_3Se_4		61
	Trüstedtite	Ni_3Se_4		61
	Kullerudite	$NiSe_2$		61
	Sederholmite	β-NiSe		61
	Mäkinenite	γ-NiSe		61
Ni–Cu–Co	Tyrrellite	$(Cu,Co,Ni)_2Se_4$		
Co	Trögtalite	$CoSe_2$		
	Hastite	$CoSe_2$		
	Bornhardtite	Co_3Se_4		
	Freboldite	CoSe(?)		
Bi	Guanajuatite	$Bi_2(Se, S)_3$	Frenzelite, castillite, bismuth selenide, selenobismuthite	
	Paraguanajuatite	Bi_2Se_2S		
	Laitakariite	$Bi_8(S,Se)_7$(?)		
As	Jermoite	$As(S,Se)_2$		
Pd	Palladium selenide			
		III. Sulfosalts		
Pb–Bi	Weibullite	$PbBi_2(S,Se)_4$		
	Platynite	$PbBi_2(Se,S)_3$		
	Wittite	$[Pb_5Bi_6(Se,S)_{14}(?)]$ or $5PbS \cdot 3Bi_2(Se,S)_3$		
		IV. Oxides		
	Selenolite	SeO_2		
		V. Oxyacid Salts		
Pb	Kerstenite	$PbSeO_4 \cdot 2H_2O$	Glasbachite, selenocerussite	
	Molybdomenite	$PbSeO_3 \cdot nH_2O$		
Cu	Chalcomenite	$CuSeO_3 \cdot 2H_2O$		
Fe	Iron selenites	?		
Hg	Mercury selenite	?		
Ni	Ahlfeldite	$NiSeO_3 \cdot 2H_2O$		
Co	Cobaltomenite			

Table 1.

roasting the muds with soda or sulfuric acid, or by smelting them with soda and niter.

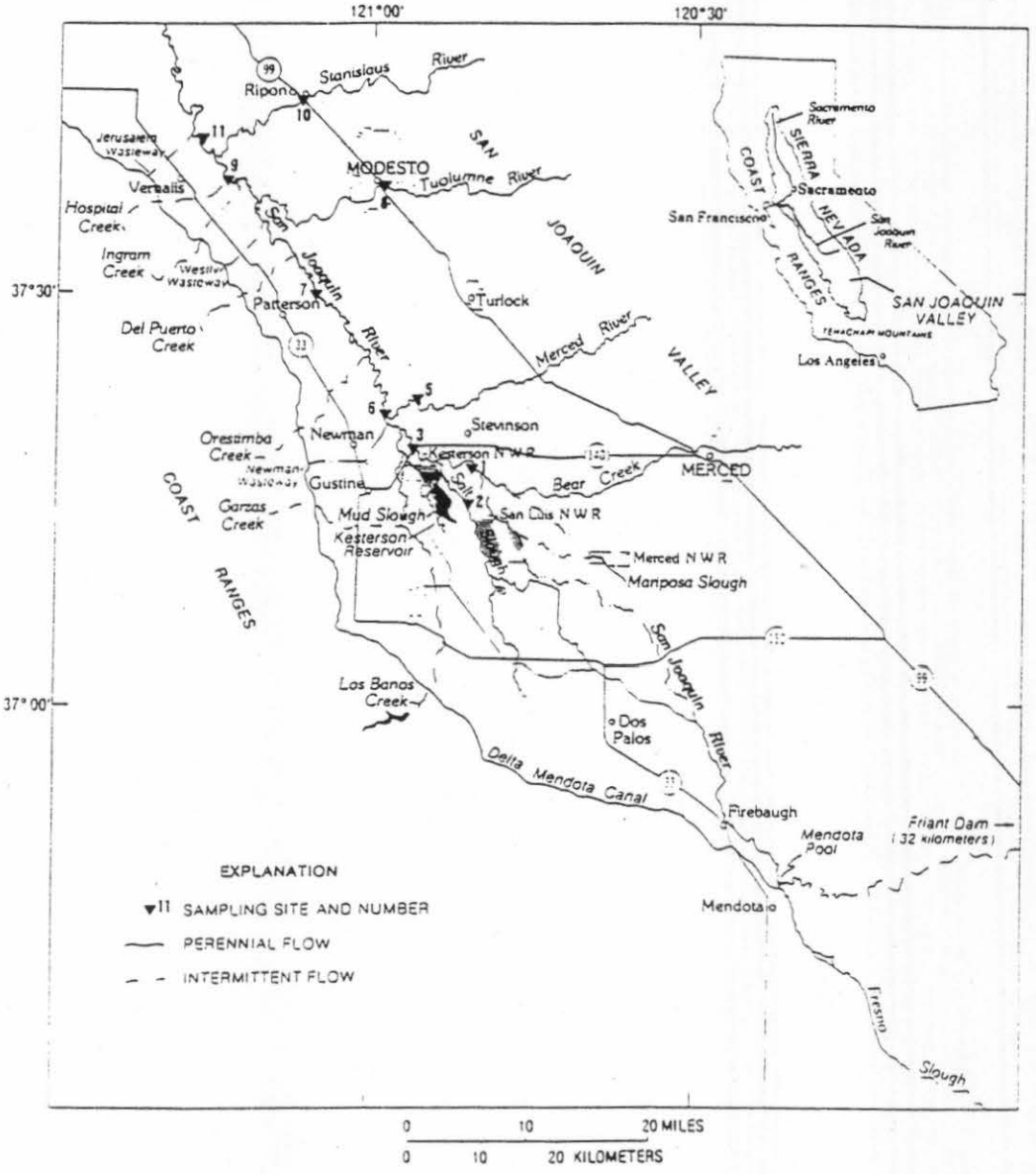
Selenium exhibits both photovoltaic action, where light is converted directly into electricity, and photoconductive action, where the electrical resistance decreases with increased illumination. These properties make selenium useful in the production of photocells and exposure meters for photographic use, as well as solar cells. Selenium is also able to convert a.c. electricity to d.c., and is extensively used in rectifiers. Below its melting point selenium is a p-type semiconductor and is finding many uses in electronic and solid-state applications [19]. It is used in Xerography for reproducing and copying documents, letters, etc. It is used by the glass industry to decolorize glass and to make ruby-colored glasses and enamels. It is also used as a photographic toner, as an additive to stainless steel and vulcanizing rubber [41].

SECTION II. CASE STUDY

The Kesterson National Wildlife Refuge

One example of just how serious an impact selenium enrichment can have has been well documented in California. The Kesterson National Wildlife Refuge (KNWR) was the terminus for the 84 mile long cement-lined San Luis Drain. See Map 1. This

MAP 1. The Kesterson National Wildlife Refuge

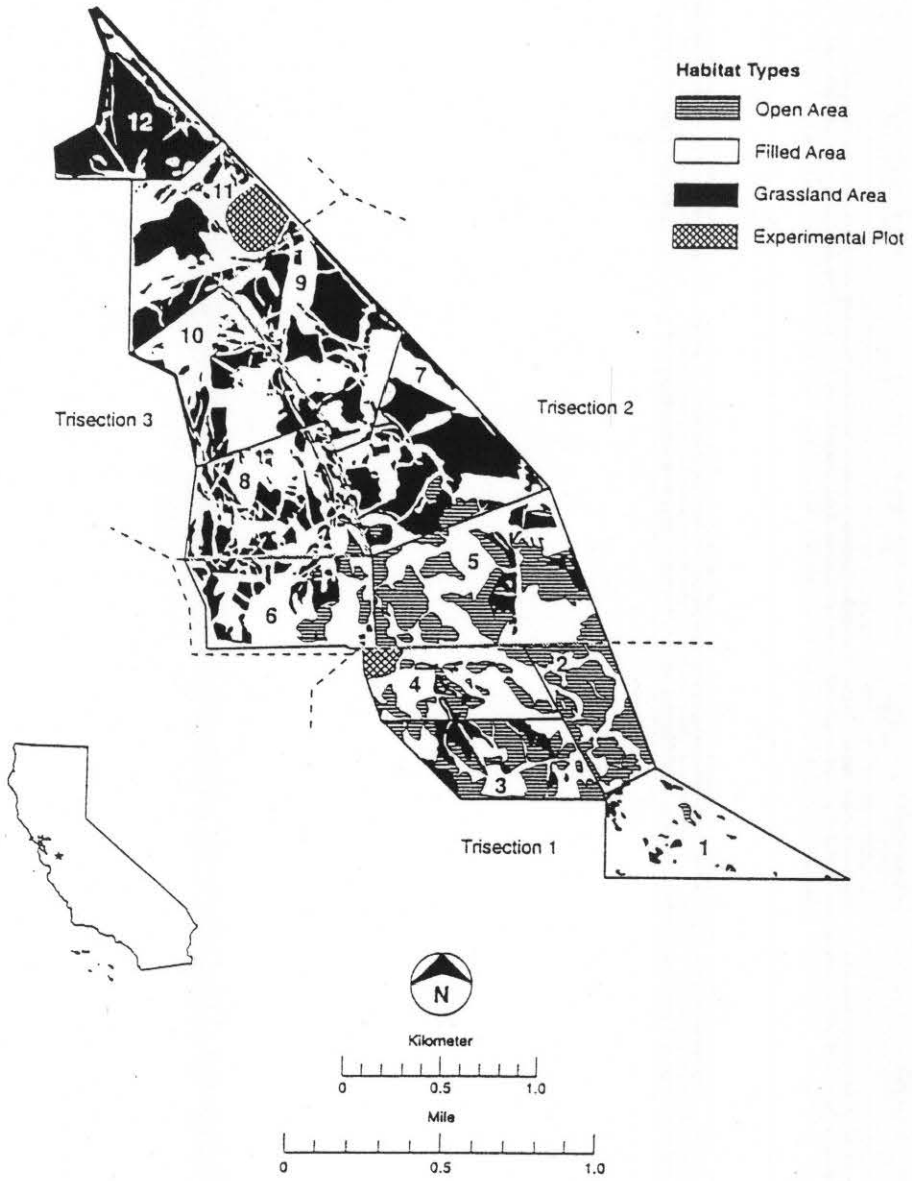


Map 1.

drain transported irrigation effluents of some 77,000 acres of farmlands into the San Joaquin River, which feeds the KNWR [13]. The KNWR was a place where the saline drainage could temporarily be managed by reducing its volume through evaporation and percolation through unlined pond bottoms. The San Luis Drain was to initially run all the way to the Sacramento-San Joaquin Delta, just upstream of the San Francisco Bay. But, before the U.S. Bureau of Reclamation could complete the plumbing, and then discharge those flows to the delta, a discharge permit was needed from California's State Water Resources Control Board. And that agency had ordered a full round of water quality testing to look for adverse environmental and biological impacts from agricultural drainwater and to detect changes in the water quality of the marsh and the health of its aquatic-based food chain. It was the result of these samplings in 1983 that first alerted the authorities to one of the worst cases of selenium toxicity in this country [15]. At first, aquatic birds nesting at the Kesterson Reservoir were found to have high rates of embryo deformities and mortalities [1, 2]. High numbers of deaths for adult birds were also found. After more testing and assessment, it was found that various other species were experiencing potentially harmful effects. The effects of selenium toxicity range from physical malformations during embryonic development to sterility to death.

The Division of Reclamation of California undertook studies and control actions to help to alleviate the hazards of the toxic

levels of selenium to the aquatic birds. They halted the discharge of agricultural drainage to the Kesterson in 1986 and in 1988 they dewatered the Reservoir and filled all the areas to at least 15 cm above the expected average seasonal rise of groundwater [27]. These actions of drying and filling the Kesterson Reservoir essentially transformed the Reservoir into three types of terrestrial habitats. The Grassland habitat includes the higher elevation upland area that existed at the reservoir before it was dried and filled; Filled habitat includes formerly low-lying areas filled with soil to prevent the occurrence of seasonal wetlands; and Open habitat includes former cattail areas that were not filled but were disked. The grassland habitat covers roughly 30% of the reservoir, filled habitat about 60%, and open habitat, about 10% [27]. See Map 2. The results of these remediation steps are still being monitored today.



MAP 2. KNWR Remediation Layout

Factors Contributing to High Levels of Selenium.

The Geochemical Processes

To the East, the valley is bounded by the Sierra Nevada Mountains. The Sierras are primarily composed of Pre-Triassic Granitic rocks and metamorphosed sedimentary rocks. The Tehachapi Mountains, to the south, are composed primarily of granitic rocks. The coast Range, lying to the west of the valley, is an assemblage of Late Jurassic to Late Cretaceous and partly Mesozoic ultramafic rocks. These rocks are overlain by Cretaceous and Triassic marine rocks. To the north is the Sacramento Valley which combined with the San Joaquin Valley, composes what is known as the Great Central Valley.

Structurally, the San Joaquin Valley forms a trough with 3000 feet of unconsolidated deposits of sediments, with underlying clay lenses. These sediments are mainly composed of alluvial fan, flood plain, flood basin, lacustrine, and marsh deposits from the surrounding features.

Selenium is prevalent in the soils of the western United States and in the San Joaquin Valley due to the weathering of many exposed Cretaceous rocks. The primary reasons for the enrichment of selenium in Cretaceous sediments and soils are attributed to extensive volcanism and the deposition of marine rocks that occurred in that time period. A period of major mountain building commenced in the Jurassic, culminating the Cordilleran orogeny. This orogeny, which spanned from the Late Jurassic to the Early Cenozoic time, produced the extensive

volcanism. With this, large emanations of sulfur accompanied by selenium, a chalcophile element, were released.

Another cause of selenium enrichment in the soils is due to the weathering of marine shales and carbonates, also of Cretaceous age. Argillaceous marine sediments show that selenium is already somewhat enriched in the hydrolyzates. In the oxidate sediments the degree of enrichment is still higher. This is caused by the fact that freshly precipitated hydroxides of Fe^3 and Mn^4 are able to adsorb selenium nearly quantitatively from aqueous solutions. Selenium thus is removed from sea water in the manner similar to that of arsenic, chiefly with depositing oxidates ("depoisoning" of ocean water). A part of selenium is removed during the precipitation of the carbonate sediments; but the evaporates are nearly devoid of selenium [4].

The Hydrologic Processes

Selenium is incorporated into the biosphere when these source rocks are exposed to rainfall, sunlight, and oxygen. They chemically weather from insoluble selenide into two forms of poison: water soluble selenate and insoluble selenite, which moves with compounds of iron and aluminum. These forms are then transported to the valley floor, where selenate moves into the water column. Due to the extensive irrigation throughout most of the San Joaquin Valley, a shallower water table is produced. Thus the selenate moves, through the ground water and capillary action into the upper soils where evapotranspiration takes place

causing it to become further concentrated at the surface. The selenite, once into the cultivated and irrigated alkaline soils, further weathers and progresses to water soluble sodium selenate salts and appears as crusts within the valley soils via the same processes [6,7]. Also, the use of phosphate fertilizers, which can contain at least some selenium, can contribute to the overall effect of higher concentrations of selenium in the soils.

The Aquatic/Ecologic Cycle

Selenium becomes further concentrated through its aquatic cycle [13], as shown from examples like the Kesterson National Wildlife Refuge. See Figure 2.

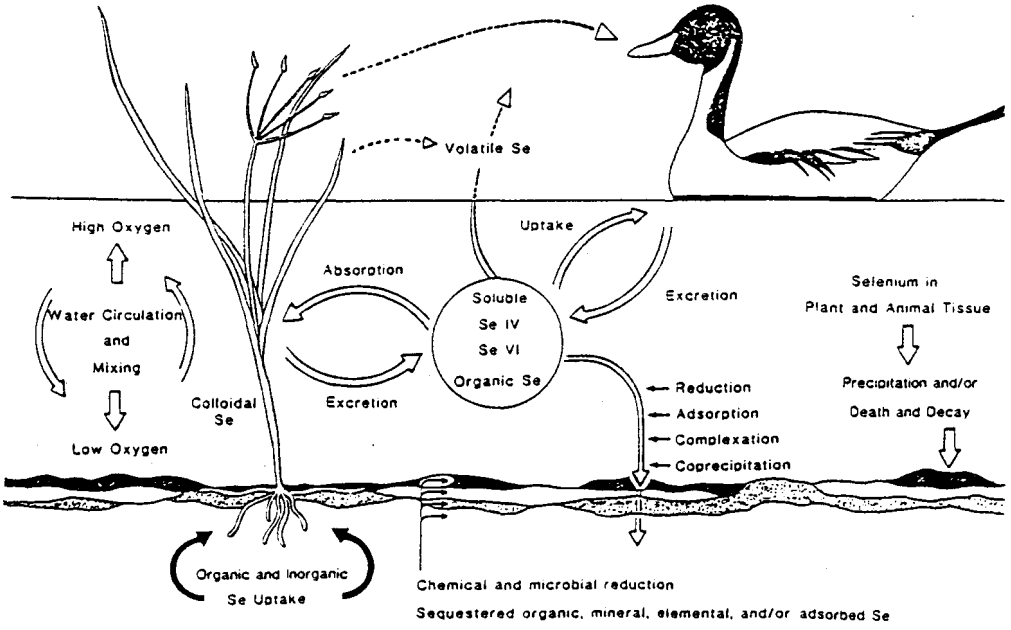


FIGURE 2. Aquatic Cycle of Selenium

Processes for the immobilization of selenium. From The United States Department of the Interior-Fish and Wildlife Service Fish and Wildlife Leaflet 12. (1987)

Selenium can be removed from solution and sequestered in sediments through the natural processes of chemical and microbial reduction from selenate (VI) to selenite (IV), followed by adsorption (binding and complexation) onto clay and the organic carbon phase of particulates, reaction with iron species, and coprecipitaiton or settling. Regardless of the route, once selenium is in the sediments, further chemical and microbial reduction may occur, resulting in insoluble organic, mineral, elemental, or adsorbed selenium. Most selenium in animal and plant tissues is eventually deposited as detritus and, over time, is isolated through the process of sedimentation. Some selenium, particularly certain organic forms, may be released into the atmosphere through volatilization by chemical or microbial activity in the water and sediments, or through direct release by plants. This can return again through precipitation of rain or snow. In total, immobilization processes effectively remove selenium from the soluble pool, especially in slow moving or still water habitats and wetlands, such as the KNWR. Ninety percent of the total selenium in an aquatic system may be in the upper few centimeters of sediment and overlying detritus.

Selenium in sediments is particularly important to long-term habitat quality because mechanisms present in most aquatic systems effectively mobilize such selenium into food chains and thereby cause long-term dietary exposure to fish and wildlife.

Selenium is made available for biological uptake by four major processes. The first is the oxidation and methylation of

inorganic and organic selenium by plant roots and microorganisms. The second process is the biological mixing and associated oxidation of sediments that results from the burrowing of benthic invertebrates and feeding activities of fish and wildlife. The third process is represented by physical perturbation and chemical oxidation associated with water circulation and mixing (current, wind, stratification, precipitation, and upwelling). Finally, sediments may be oxidized by plant photosynthesis.

Two additional pathways provide for direct movement of selenium from sediments into food chains, even when the surface water does not contain the element. These pathways are uptake of selenium by rooted plants and uptake by bottom-dwelling invertebrates and detrital-feeding fish and wildlife. These two pathways may be the most important in the long-term cycling of potentially toxic concentrations of selenium. Thus, rooted plants and the detrital food pathway can continue to be highly contaminated and expose fish and wildlife through dietary routes even though concentrations of selenium in water are low. This process is known as biomagnification [28].

These combined effects of both naturally occurring geochemical and biological cycles and man-made irrigation processes have been the major contributors to the accumulation of selenium and the toxic effects seen in the Kesterson National Wildlife Refuge.

SECTION III. SELENIUM TOXICITY

Selenium is widely used as a therapeutic agent by veterinarians to remedy eczema and fungal infections and as a necessary micronutrient to treat everything from white muscle disease in livestock to exudative diathesis, a similar ailment, in chicks. High concentrations of selenium can cause acute toxic effects to many rudimentary organisms in the environment. Elemental selenium has been said to be practically nontoxic and is considered to be an essential trace element; however, hydrogen selenide and other selenium compounds are extremely toxic, and resemble arsenic in their physiological reactions. Hydrogen selenide in a concentration of 1.5 ppm is intolerable to man. Selenium occurs in some soils in amounts sufficient to produce serious effects on animals feeding on plants, such as locoweed, grown in such soils. Exposure to selenium compounds (as Se) in air should not exceed 0.2 mg/m3 (8-hour time-weighted average---40 hour week).

The Federal Standard for Drinking Water in the United States is 0.01 ppb (U.S. EPA, 1986). See Figure 3. Drainwater flowing

FIGURE 3.

Federal Standards for Drinking Water

Element/ Compound	Sources	National Drinking Water Standard (mg/l)
Arsenic	Runoff, mining, smelters, pesticides	0.05
Asbestos[a]	Industrial, wallboard, insulation, talc	
Barium	Clinical tests, radiation testing	1.0
Beryllium[b]	Acid mine drainage, industrial, natural	0.5 Recom. for irrigation water
Cadmium	Industry, mining, pesticides	0.01
Chromium	Industrial	0.05
Copper	Industrial	1.0
Lead	Mining, industry, autos, pesticides	0.05
Manganese	Mining	0.05
Mercury	Mining, seed dressing, natural	
Nickel	Mining, oxide powder, sulfides	
Selenium	Agricultural runoff, mining	0.01
Zinc	Industrial	5.0
Arsenicals	Lead arsenates	
Silica gels	Aerosols, dessicants	

From ReVelle and ReVelle 1974. Sourcebook on the Environment—the Scientific Perspective. Houghton Mifflin, Boston, pp. 62–64. Permission granted.

[a] *Carcinogen*

[b] *lung disease*

into the Kesterson marsh averaged 290 ppb of selenium. That was more than 8 times above the Environmental Protection Agency standard of 35 ppb to protect freshwater aquatic species. The EPA later changed that safety number to 5 ppb when it learned that selenium is 5 times more poisonous than arsenic. The highest concentration of selenium ever recorded in California occurred in a sump entering into the Kesterson National Wildlife Refuge, it contained 4,200 ppb selenium. The EPA and California constitutes a liquid containing greater than 1,000 ppb selenium a hazardous waste.

Humans

In humans, the Federal Drug Administration has determined ill effects in amounts of 0.8-1.0 ppm. The National Institute of Health indicate poisoning starts at 0.5 ppm and severe toxicity at 3 ppm. The Recommended Daily Allowances of selenium are 76 ug for males, 50 ug for females, and 10 ug for infants. See Table 2.

TABLE 2. Recommended Daily Allowances of Selenium

Group	Age (years)	Daily selenium intake (ug)
Infants	0 - 0.5	10 - 40
	0.5 - 1	20 - 60
Children	1 - 3	20 - 80
	4 - 6	30 - 120
	7+	50 - 200
Adults		50 - 200

[1] Adapted from: US NAS/NRC (1980).

Symptoms of selenium intoxication can include benign skin sores, lethargy, hair loss, numbing or tingling effects in the extremities, headaches, dizziness, garlic odor on breath, and motor disturbances. However, more studies in this area are needed.

Plants

Plants are one organism that manages to bioaccumulate selenium to a tremendous amount. There are three categories of plant accumulators. First there are obligate plants that grow where soils contain enough selenium to support the metabolic needs of the plant. These plants are noted as primary indicators of selenium rich soils. They include the species *Astragalus, Machaeranthera, Haplopappus*, and *Stanleya*. These plants can concentrate selenium by a factor of 1000. The second category is the facultative plants which can accumulate selenium in their tissues but can also grow in soils that contain little or no selenium. These include the *Atriplex, Grindelia,* and *Grayia*. These plants can concentrate selenium by a factor of 100. The third category is the non-accumulator plants which concentrate selenium by a factor of 1-10 [16,41].

Much of the selenium in crop plants is associated with the protein and its distribution in the plant relates in a general way to the distribution of protein, being higher in the seeds than in the straw [21].

Wildlife

The toxicity of selenium in animals is influenced by several factors. Among these are the animal species, the composition of the ration, the chemical form of the selenium, the concentration of the element and the duration of intake. The most likely form of selenium toxicity to fish, wildlife, livestock and humans is through bioaccumulation. Bioaccumulation is the ability of organisms to accumulate an element to concentrations one or more orders of magnitude greater than the concentrations in the water or food it receives. Because the KNWR was a marshy, stagnant area, the conditions for accumulation and toxicity were ideal.

Fish tissues readily bioaccumulate selenium [34]. The mean length of bluegills of age 1 were shorter in rivers containing higher concentrations of selenium than in rivers with low concentrations. Reported concentrations of selenium in water exceeding 2-5 ppb may cause reproductive failure or mortality in fishes (bluegills) because of bioconcentration in the food chain. Mean environmental concentrations of approximately 25 ppb may seriously affect reproduction capacity of perch, but no clear effects on reproduction are evident at mean concentrations of 10 ppb and below [22]. There was only limited impact on the invertebrate community at 25 ppb [18]. Selenium induced effects occur during gametogenesis, but only become evident between fertilization and hatching [25].

The most common deformities in chicks are missing or short upper beaks, missing eyes, deformed feet and legs, edema of the

head and neck, and a wiry down which gives those chicks that do hatch a greased appearance. Egg production is delayed and hatchability is reduced. In the Kesterson, forty percent of the nests checked contained one dead embryo, twenty percent yielded at least one embryo or chick with multiple deformities. Forty-one percent of all the nesting birds suffered some form of reproductive failure [15]. The reasons for these effects on embryonic development are due to selenium's affinity for protein, which is the major constituent of eggs and sperm.

Three types of selenium poisoning in livestock have been noted: (1)acute, (2) chronic, blind staggers, and (3) chronic, alkali disease [32]. The acute poisoning results when plants of high selenium content such as the primary indicator plants, are consumed in sufficient quantity. The symptoms are severe, including abnormal movement and posture, watery diarrhea, elevated temperature and pulse rate, labored breathing, prostration and often death from respiratory failure. The blind staggers type of chronic selenium poisoning results from the consumption of primary indicator plants in limited amounts over a considerable period of time. In early stages of the poisoning, cattle wander, stumble, appear to have impaired vision, and lose their appetite for food and water. Later their front legs become weak, and finally paralysis and respiratory failure precede death. Chronic selenium poisoning of the alkali disease type results from the continuous ingestion of feeds that contain over 5 but usually less than 40 ppm of selenium. This occurs in

horses, cattle, and swine with varying symptoms [21,41].

SECTION IV. THE GENERAL CHEMISTRY OF SULFUR AND TELLURIUM AND THEIR TOXICITIES.

General Chemistry of Sulfur

Sulfur (chemical symbol of S) has an atomic weight of 32.066 grams per mole and an atomic number of 16. Sulfur is a pale yellow, odorless, brittle solid, which is insoluble in water but soluble in carbon disulfide. In every state, whether gas, liquid or solid, elemental sulfur occurs in more than one allotropic form or modification; these present a confusing multitude of forms whose relations are not yet fully understood. Amorphous or "plastic" sulfur is obtained by fast cooling of the crystalline form. X-ray studies indicate that amorphous sulfur may have a helical structure with eight atoms per spiral. Crystalline sulfur seems to be made of rings, each containing eight sulfur atoms, which fit together to give a normal X-ray pattern. Eleven isotopes of sulfur exist. Four occur in natural sulfur, none of which is radioactive. A finely divided form of sulfur, known as flowers of sulfur, is obtained by sublimation. Sulfur readily forms sulfides with many elements.

Sulfur occurs native in the vicinity of volcanoes and hot springs. In sulfur's anionic form of -2, sulfide is widely distributed in nature in iron pyrites, galena, sphalerite, cinnabar, stibnite, gypsum, Epsom salts, celestite, barite, etc. See Table 3 for other sulfur containing minerals. Sulfur is commercially recovered from wells sunk into the salt domes along the Gulf Coast of the U.S. It is obtained from these wells by

TABLE 3. Sulfur Bearing Minerals[1]

Mineral Name	Composition	Sulfur Content (%)	System
	Sulfides		
Argentite	Ag_2S	12.9	Isometric
Arsenopyrite	$FeAsS$	19.7	Orthorhombic
Bismuthinite	Bi_2S_3	18.8	Orthorhombic
Bornite	Cu_5FeS_4	25.5	Isometric
Bravoite	$(Ni,Fe)S_2$	~36	Isometric
Chalcocite	Cu_2S	20.2	Orthorhombic
Chalcopyrite	$CuFeS_2$	35.0	Tetragonal
Cinnibar	HgS	13.8	Trigonal
Cobaltite	$CoAsS$	19.3	Isometric
Covellite	CuS	33.6	Hexagonal
Cubanite	$CuFe_2S_3$	35.4	
Digenite	$Cu_{2-x}S$	<20	Orthorhombic
Dimorphite	As_4S_7	24.3	
Galena	PbS	13.4	Isometric
Greenockite	CdS	22.2	Hexagonal
Greigite	Fe_3S_4	43.4	Isometric
Mackinawite	FeS	34.1	Tetragonal
Marcasite	FeS_2	53.4	Orthorhombic
Molybdenite	MoS_2	40.1	Hexgonal
Oldhamite	CaS	44.4	Isometric
Orphiment	As_2S_3	39.0	Monoclinic
Pentlandite	$(Fe,Ni)_9S_8$	~36	Isometric
Pyrite	FeS_2	53.4	Isometric
Pyrrhotite	$Fe_{1-x}S$	~36	Hexagonal
Realgar	AsS	29.9	Monoclinic
Sphalerite	ZnS	33.0	Isometric
Stibnite	Sb_2S_3	28.6	Orthorhombic
Stannite	Cu_2FeSnS_4	29.8	Tetragonal
Troilite	FeS	36.5	
Tungstenite	WS_2	25.9	Hexagonal
Violarite	Ni_2FeS_4		Isometric
	Sulfosalts		
Andorite	$PbAgSb_3S_6$	22.0	—
Argyrodite	Ag_8GeS_6	17.1	Isometric
Boulangerite	$Pb_5Sb_4S_{11}$	18.9	Monoclinic
Bournonite	$PbCuSbS_3$	19.7	Orthorhombic
Chalcostibite	$CuSbS_2$	25.7	Orthorhombic
Cosalite	$Pb_2Bi_2S_5$	16.2	—
Enargite	Cu_3AsS_4	32.6	Orthorhombic
Livingstonite	$HgSb_4S_7$	24.6	—
Plagionite	$Pb_5Sb_8S_{17}$	21.3	Monoclinic
Polybasite	$(Ag,Cu)_{16}Sb$	~17.9	Monoclinic
Proustite	Ag_3AsS_3	19.4	Trigonal
Pyrargyrite	Ag_3SbS_3	17.8	Trigonal
Sulvanite	Cu_3VS_4	34.7	Isometric
Tennantite	$(CuFe,Zn,Ag)_{12}As_4S_{13}$	~28	Isometric
Tetrahedrite	$(Cu,Fe,Zn,Ag)_{12}Sb_4S_{13}$	~25	Isometric
Native sulfur	S	100	Orthorhombic
	Sulfates		
Alum	$(K,Na,NH_4)Al(SO_4)_2 \cdot 12H_2O$	~39.9	Isometric
Alunite	$KAl_3(SO_4)_2(OH)_6$	15.4	Trigonal
Anglesite	$PbSO_4$	10.6	Orthorhombic
Anhydrite	$CaSO_4$	23.5	Orthorhombic
Barite	$BaSO_4$	13.7	Orthorhombic
Bloedite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$	19.2	Monoclinic
Brochantite	$Cu_4(SO_4)(OH)_6$	7.1	Monoclinic
Celestite	$SrSO_4$	17.4	Orthorhombic
Copiapite	$CuSO_4 \cdot 5H_2O$	12.8	Triclinic
Epsomite	$MgSO_4 \cdot 7H_2O$	13.0	Orthorhombic
Gypsum	$CaSO_4 \cdot 2H_2O$	18.6	Monoclinic
Halotrichite	$Fe(II)Al_2(SO_4)_4 \cdot 22H_2O$	14.4	Monoclinic
Hexahydrite	$MgSO_4 \cdot 6H_2O$	14.0	Monoclinic
Jarosite	$KFe_3(SO_4)_2(OH)_6$	12.8	Trigonal
Kainite	$KMg_4(SO_4)Cl \cdot 3H_2O$	12.9	Monoclinic
Kieserite	$MgSO_4 \cdot H_2O$	23.2	Monoclinic
Langbeinite	$K_2Mg_2(SO_4)_3$	23.2	Isometric
Mascagnite	$(NH_4)_2SO_4$	24.3	Orthorhombic
Melanterite	$FeSO_4 \cdot 7H_2O$	11.5	Monoclinic
Mendozite	$NaAl(SO_4)_2 \cdot 11H_2O$	14.6	Monoclinic
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	10.0	—
Polyhalite	$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$	21.2	Triclinic
Picromerite	$K_2Mg(SO_4)_2 \cdot 6H_2O$	15.9	Monoclinic
Thenardite	Na_2SO_4	22.6	Orthorhombic

[1] Based mostly on the compilation by Staples (1972).

the Frasch process, which forces heated water into the wells to melt the sulfur, which is then brought to the surface. Sulfur also occurs in natural gas and petroleum crudes and must be removed from these products. Large amounts of sulfur are being recovered from Alberta gas fields.

Sulfur is a component of black gunpowder and is used in the vulcanization of natural rubber and as a fungicide. It is also used extensively in making phosphatic fertilizers. A tremendous tonnage is used to produce sulfuric acid, the most important manufactured chemical. It is used in making sulfite paper and other papers, as a fumigant, and in the bleaching of dried fruits. The element is a good electrical insulator. Organic compounds containing sulfur are very important. Calcium sulfate, ammonium sulfate, carbon disulfide, sulfur dioxide, and hydrogen sulfide are but a few of the many other important compounds of sulfur.

Sulfur Toxicity

In humans and most organisms, sulfur is essential to life. Sulfur is a characteristic constituent of enzymes and proteins and a key constituent in metabolic roles. It is a minor constituent of fats, body fluids, and skeletal minerals, and an essential component of many biochemical and inorganic systems in nature [8].

The flow of sulfur within and through aquatic ecosystems is very important. The geochemical mobility in any given situation

is determined by the oxidation state of the sulfur, the biological productivity, and the synergistic effects of the other elemental and nutrient cycles. In the biosphere, there is a strong link between the biogeochemical cycles of six major elements of which sulfur is one and the others are carbon, hydrogen, oxygen, nitrogen and phosphorus. There are three major ways in which these elements interact. These elements combine together as biochemical components of living organisms by photosynthesis and other chemosynthetic processes [24]. They are transformed together by respiration and catabolism or released together as waste products. Or these elements are biodegraded into varius organic and inorganic products. The interactions between inorganic and organic sulfur can be seen in Figure 4. The sulfur cycle itself operates with two different groups of bacteria, the aerobic sulfur-oxidizing bacteria and the anaerobic sulfur-reducing bacteria. The bacteria functioning in excess would be determined on the conditions of the environment, either acidic or alkaline [20].

Carbon disulfide, hydrogen sulfide, and sulfur dioxide should be handled carefully. Hydrogen sulfide in small concentrations can be metabolized, but in higher concentrations it quickly can cause death by respiratory paralysis, similar to hydrogen selenide. It is insidious in that it quickly deadens the sense of smell. Sulfur compounds such as sulfuric acid and various sulfates also cause toxic effects to mucus membranes and to the lungs [20]. Sulfur dioxide is a dangerous component in

atmospheric air pollution, which it is most often associated with due to increasing public awareness [5]. Although the complete impact of sulfur in air pollution is still under debate.

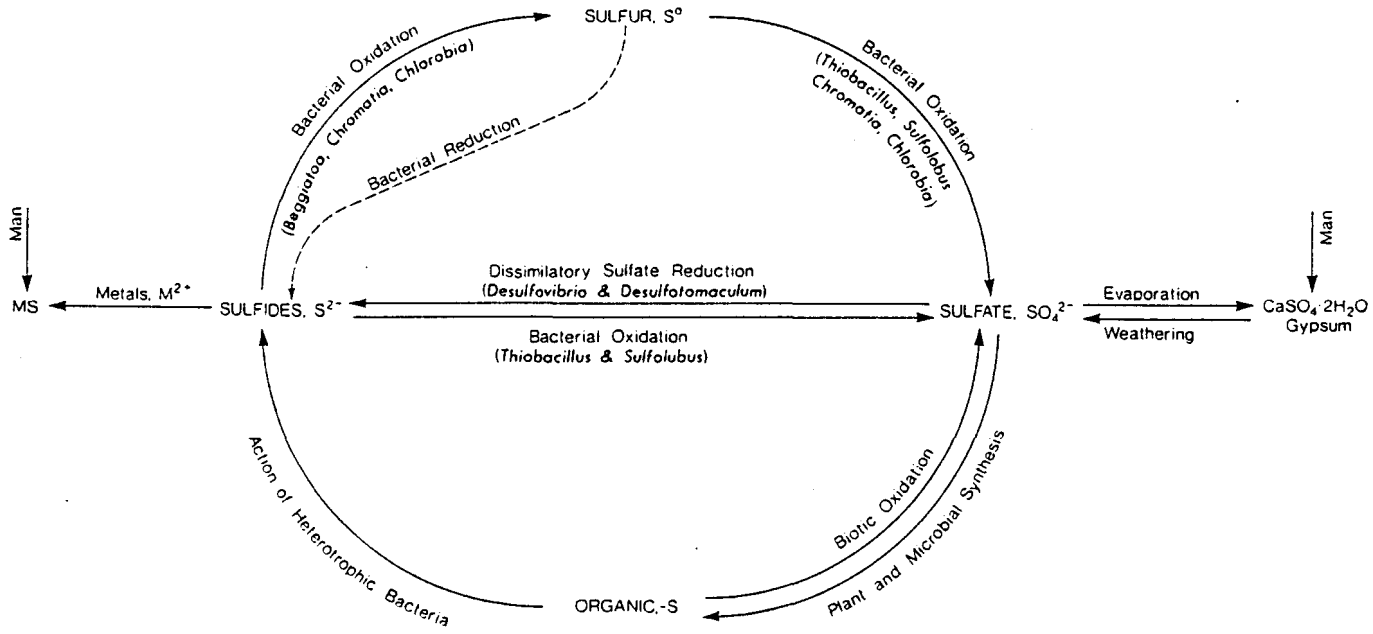


FIGURE 4. Sulfur Cycle

General Chemistry of Tellurium

Tellurium (chemical symbol of Te) has an atomic weight of 127.60 and an atomic number of 52. It was discovered by Muller von Reichenstein in 1782. There are two allotropic forms of elemental tellurium, amorphous and crystalline [2]. The amorphous form is brown. Amorphous tellurium is formed by precipitating tellurium from a solution of telluric or tellurous acid. Whether this form is truly amorphous, or made of minute crystals, is open to question. Crystalline tellurium has a silvery-white appearance, and when pure exhibits a metallic appearance and is isomorphous with gray selenium B. It is brittle and easily pulverized. In air, tellurium burns with a greenish-blue flame, forming the dioxide. Tellurium dioxide reacts with halogens, but not sulfur or selenium. In its anion form with a -2 charge, telluride resembles selenide, and the cation form of +4, it resembles platinum (IV). Thirty isotopes of tellurium are known, with atomic masses ranging from 108 to 137. Natural tellurium consists of eight isotopes.

Tellurium is occasionally found native, but is more often found in the telluride of gold (calaverite), and combined with other metals. It occurs with selenium in sulfur deposits in Japan and is found as free element in central Europe, Colorado, and Bolivia. Some tellurides or tellurium bearing minerals are telluride sylvanite (graphic tellurium), $(Ag,Au)Te_2$; nagyagite (black tellurium), $(Ag,Pb)_2(Te,S,Sb)_3$; hessite, Ag_2Te; tetradymite, Bi_2Te_3; altaite, PbTe; coloradoite, HgTe; and other

silver-gold tellurides [20]. It is recovered commercially from the anode muds produced during the electrolytic refining of blister copper. The U.S., Canada, Peru and Japan are the largest Free World producers of the element.

Tellurium is a p-type semiconductor, and shows greater conductivity in certain directions, depending on alignment of the atoms. The electrical conductivity of tellurium is extremely low and is increased by the presence of small quantities of impurities. Its conductivity increases slightly with exposure to light. It can be doped with silver, copper, gold, tin, or other elements. Molten tellurium corrodes iron, copper, and stainless steel. Telluium improves the machinability of copper and stainless steel, and its addition to lead decreases the corrosive action of sulfuric acid on lead and improves its strength and hardness. Tellurium is used as a basic ingredient in blasting caps, and is added to cast iron for chill control. Tellurium is used in ceramics. Bismuth telluride has been used in thermoelectric devices [19].

Tellurium Toxicity

Tellurium and its compounds are probably toxic and should be handled with care. Workmen exposed to as little as 0.01 mg/m^3 of air, or less, develope "tellurium breath," which had a garlic-like odor [19]. Hydrogen telluride, a colorless gas with an even more offensive odor than hydrogen selenide, and is at least as toxic as this substance.

SECTION V. ANALYSIS OF SAMPLES FROM THE KNWR

Sample Collection

In March of 1993, I collected nine water samples and seven biological samples from the sites designated on Maps 3, 4 and 5. All the samples were taken either from the San Joaquin River itself or rivers draining into the San Joaquin. The San Joaquin River runs through the Kesterson National Wildlife Refuge. Water samples were collected and stored in 125 ml Nalgene bottles. The biological samples were collected and stored in clean plastic zip-lock baggies. These samples were labelled with the time, location, and date of collection and stored in a cooler while being transported. These samples were later prepared for analysis by an Inductivley Coupled Plasma Mass Spectrometer (ICP-MS). The ICP-MS was chosen for analyzing the samples because it is capable of performing rapid multielement analyses and because of its sensivity for the elements of sulfur, selenium, and tellurium. See Table 4 for plasma spectrometry sensitivities.

Emission spectrometry employing arc and spark sources has been used for many years as a qualitative and quantitative tool in analytical chemistry. Simultaneous multielement analysis for over 70 elements is possible with this equipment. The sensitivity available for many elements has made emission spectroscopy a popular choice for trace element analyses [39].

TABLE 4. Plasma Spectrometry Sensitivities and Detection

Detection Limits and Sensitivities of Analysis Techniques (ppb) (2)

Element	ASV detection limit	FL-AAS detection limit	ETA-AAS detection limit	ICP-AES detection limit	NAA sensitivity	X-ray fluorescence detection limit
As	—	100	0.2	20	50	—
Ba	—	200	0.06	5	20	400
Be	—	20	0.001	3	—	1000
Bi	0.05	50	0.3	50	—	2000
Cd	0.005	1	0.003	1	5	2500
Co	—	5	0.6	2	10	200
Cr	—	2	0.4	2	300	700
Cu	0.5	2	0.4	2	2	400
Fe	—	1	0.8	2	2000	300
Hg	1	2200	0.5	50	3	1000
Mn	—	3	0.1	0.5	1	200
Mo	—	10	0.2	5	1000	1500
Ni	—	8	0.1	5	700	200
Pb	0.01	10	0.05	20	500	—
Sb	0.01	30	0.2	200	7	—
Se	—	100	0.1	30	10	—
Sn	0.2	1000	0.4	3	30	—
V	—	20	0.5	2	2	150
Zn	0.4	0.6	0.02	1	100	200

Preparation of Samples

The purpose was to prepare them for analysis, using the Inductively Coupled Plasma Mass Spectrometer. In order for analysis using the ICP-MS the samples needed to be dissolved into an aqueous solution. This was done using the following procedures:

Soil Samples

All the biological samples (Sample Numbers 10E, 13B, 14B, 17 and 18) were taken out of the sample bags and placed into Teflon crucibles. These samples contained a fair amount of twigs and woody debris, of which were picked out by tweezers. The following steps were taken with each sediment sample. First the dry weight of sample was measured on a balance scale. Second, 75 ml of 6 N HCl was added to each sample. The samples were then heated on Thermolyne Hot Plate for 2 hours at 200 degrees C. There was a slight yellow colored ring observed along the interface of the solution miniscus edges and the crucible edges of crucibles. The samples were then cooled to room temperature and then filtered. The decant was placed into 250 ml volumetric flasks including two washings and diluted to volume. The diluted solutions were then transferred to 125 ml Nalgene bottles for later testing using the ICP-MS.

Water Samples

All the water samples (Sample Numbers 1-9) were filtered

using analytical grade filter paper and then placed into 50 ml Nalgene bottles with 1 ml of reagent grade HNO_3. These were then set aside until testing using the ICP-MS.

The concentrations determined for each sample by measurement using the ICP-MS at the Ohio State University can be seen on the bottom of Table 5 of the next section.

SECTION V. GRAPHICAL REPRESENTATION OF DATA.

The following graphs represent compiled data from various sources. This data was chosen as representative of various materials and then compared to each other and to the ratio of sulfur to selenium of chondrites from research by Anders and Ebihara, 1982 [1]. The reference ratio was chosen because it was the most recent data and considered to be most representative of the natural abundance of the elements involved in this study. Table 5 lists all the data, including the concentration and the material matter and the source for each data set. A log-log representation was chosen in order to make better use of the graphical relationships.

Graph 1 represents the data for various material as listed on the key. It appears that predominantly all the material is more enriched in selenium than in sulfur. This could be due to the fact that selenium is less prevalent in meteors which is what is represented by the reference line, than in environmental systems. Also, sulfur is metabolized and transformed into more into its volatile gas phases and consumed throughout more of the fundamental systems and cycles in the environment than selenium. Thus, selenium remains behind to bioaccumulate in ecological and environmental systems. It appears from the data used that if grouped together within the respective material, igneous rocks are depleted in both selenium and sulfur with respect to sedimentary rocks. This could be a result of the intense pressure and heat that form the igneous rocks liberates the

sulfur and selenium, because of their high volatility in comparison to the major components of igneous rocks. The amount of selenium in the sedimentary rocks is dependent upon the geological time and location of which they were deposited. Those bearing more selenium would be more likely to be of Cretaceous Age according to some literature. The plant material data was a compilation of a variety of plant species, none of which were indicated in one of the previous sections as a selenium bioaccumulator. Obviously, the concentrations should show differences in preferential fractionation of selenium and sulfur in the various systems of the plant. There may be more selenium in the roots as opposed to the leaf system. This was not conclusive from the graph, however due to the scatter of the data. Also, the data used was from plants grown in highly enriched selenium soils [12]. Because of the lack of data and standard testing and analysis procedures of the data, there is very little conclusive information. However, with more information involving the anaylysis for both sulfur and selenium, there could be relationships observed.

Graph 2 represents the data of Graph 1 with the addition of the concentrations of sulfur and selenium of the samples from the Kesterson National Wildlife Refuge. It appears from the graph that the samples from the KNWR are more enriched in selenium than those plants that were grown in enriched seleniferous soils. This indicates that although the KNWR has undergone remediation, the selenium levels are still very high

and cause for concern.

If a line was drawn representing the Federal Standard for drinking water, a line at 0.01 ppb or 0.00001 ppm, all the samples are greater than that allowed for drinking water. However, this relationship is not valid due to the different material used in the overall analysis.

Table 5	SULFUR	SELENIUM	UNITS	SOURCE
Earth or Crust				
crust	340	0.05	ppm	[10]
crust	260	0.05	ppm	Ahrens, 1965
Table 5				
Meteors				
chondrites	23000	8.5	ppm	Ahrens, 1965
Igneous Rocks				
andesite USGS-AGV-1	10	0.14	ppm	[11]
basalt USGS-BCR-1	392	0.1	ppm	
diabase USGS-W-1	123	0.13	ppm	
dunite USGS-DTS-1	10	0.3	ppm	
granite USGS-G-1	58	0.007	ppm	
granite USGS-G-2	24	0.7	ppm	
granodiorite USGS-GSP-1	162	0.04	ppm	
peridotite USGS-PCC-1	10	0.18	ppm	
igneous rocks	300	0.5	ppm	
Sedimentary Rocks				
oolith	2300	5.4	ppm	[14]
haematite	300	1.2	ppm	
bog-ore (Mn rich)	100	1.2	ppm	
bog ore (Mn poor)	100	0.05	ppm	
deep sea Mn nodule	2400	1.9	ppm	
anhydrite polyhalite	500000	1	ppm	
kainite	250000	1	ppm	
caliche	7700	1	ppm	
shales	2400	0.6	ppm	[3]
sandstones	240	0.05	ppm	
carbonates	1200	0.08	ppm	
deep sea sediments/clay carbonat	800	0.17	ppm	
Plants				
cock's foot	2100	28	ppm	[3]
perrenial rye grass	2300	34	ppm	
italian rye grass	1700	29	ppm	
wheat, grain	1400	39	ppm	
wheat, straw	2600	40	ppm	
oats, grain	2000	39	ppm	
oats, straw	2600	40	ppm	
barley, grain	1400	35	ppm	
barley, straw	2500	42	ppm	
lettuce	3000	56	ppm	
artichoke, leaves	1700	71	ppm	
artichoke, roots	400	19	ppm	
parsnip, leaves	2900	90	ppm	
parsnip, roots	700	22	ppm	
carrot, leaves	3100	29	ppm	
carrot, roots	900	0	ppm	
onion, leaves	1900	235	ppm	

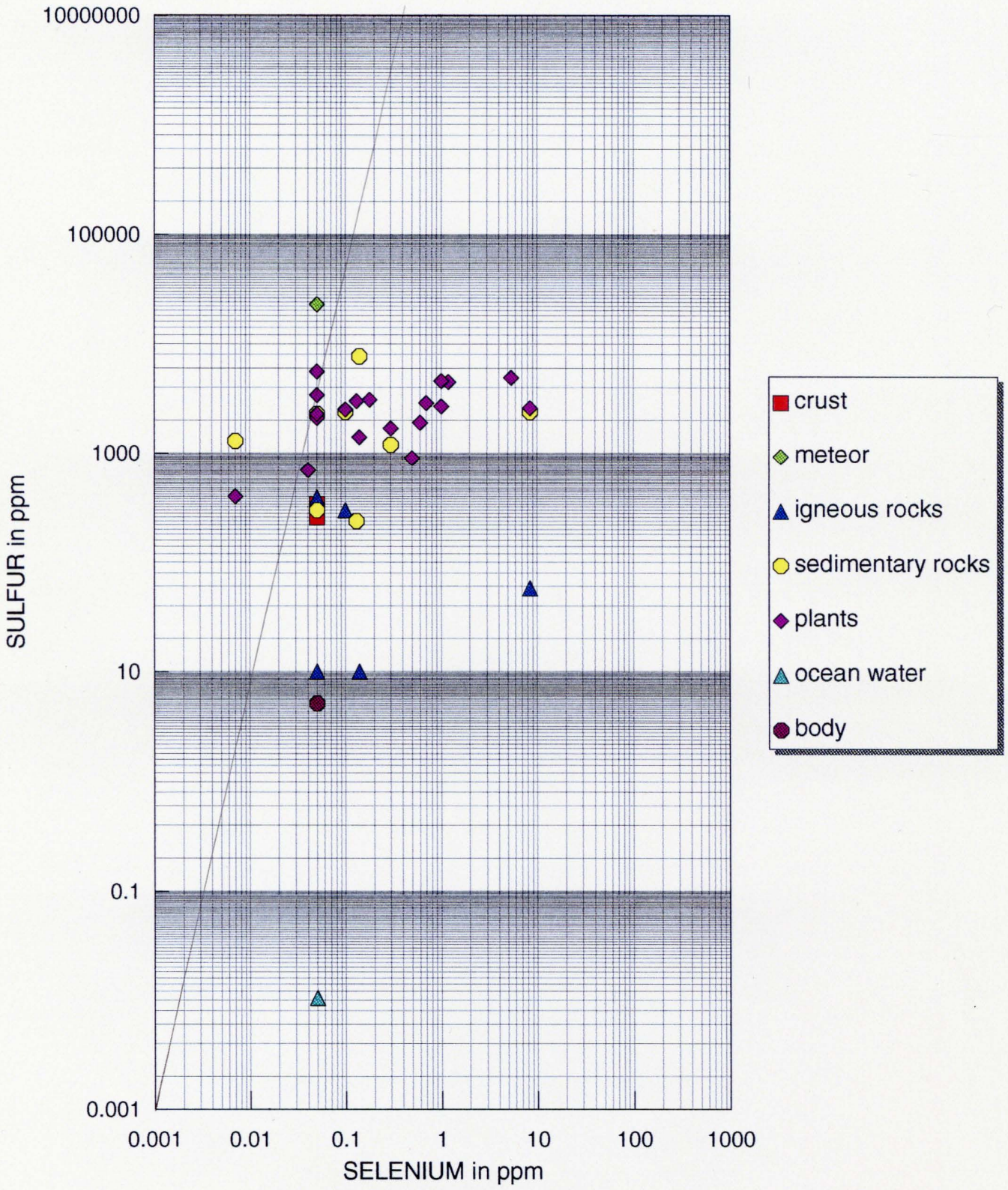
onion, bulbs	2100	82	ppm	
white clover	4900	153	ppm	
red clover	4500	103	ppm	
pea, leaves	0	79	ppm	
pea, shelled	3400	9	ppm	
radish, leaves	0	145	ppm	
radish, roots	2700	35	ppm	
cabbage, leaves	4600	196	ppm	
turnip, leaves	0	409	ppm	
turnip, roots	1900	204	ppm	
rape, leaves	5600	203	ppm	
Ocean	0.01045	0.003	mass	Bruland, 1983
Body	5.2	0	mg/kg	Bowen, 1979

Kesterson National Wildlife Refuge Area

Sample Site Number			
Water samples	1	97	0.0059
	2	44	0.0001
	3	63	0.0012
	4	700	0.0037
	5	700	0.0065
	6	700	0.018
	7	700	0.012
	8	7.4	0.0001
	9	16	0.0001
Biological samples	"10E	13	0.002
	13B	51	0.009
	14B	30	0.014
	17	15	0.0084
	18	9	0.011

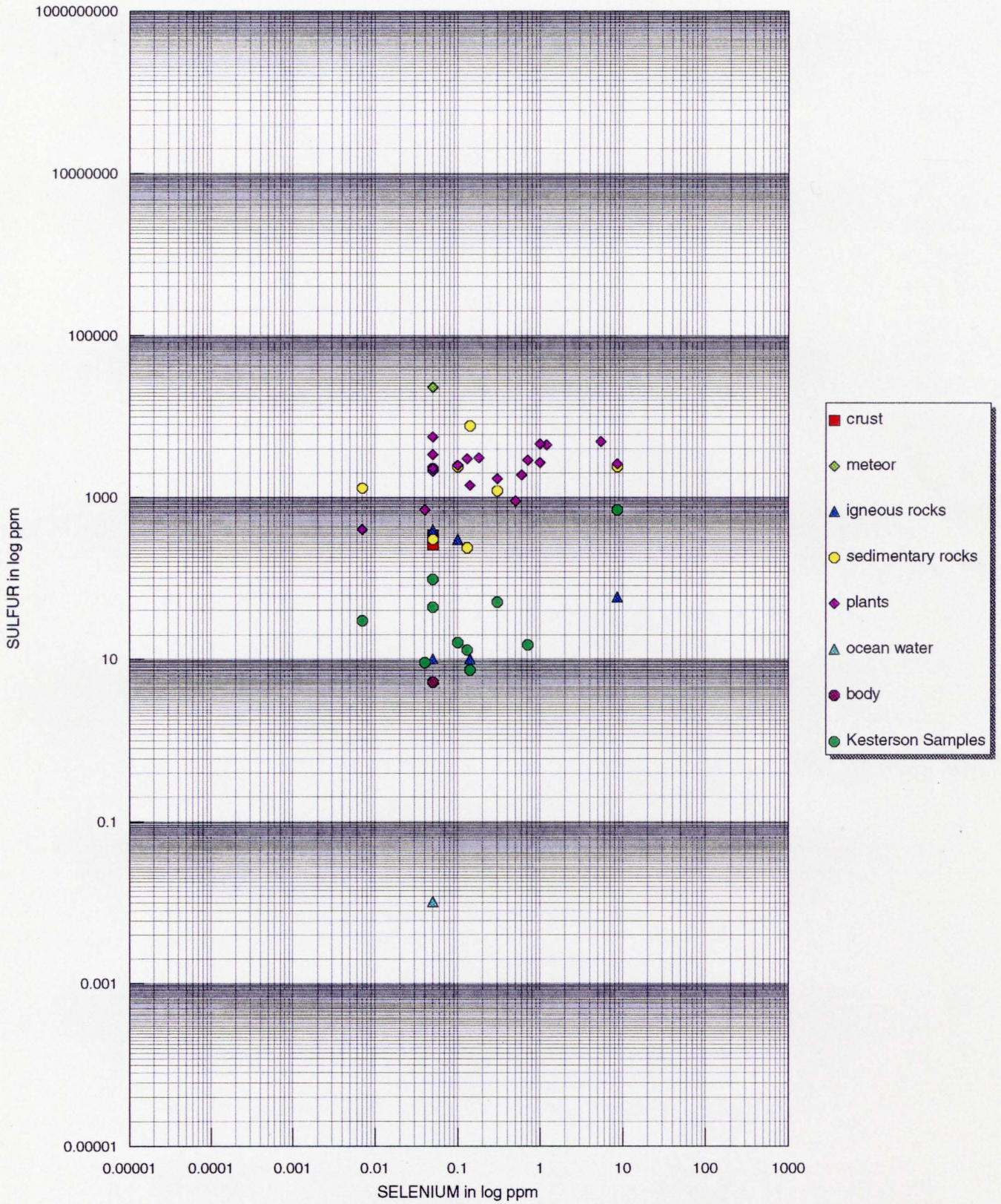
SULFUR VS. SELENIUM

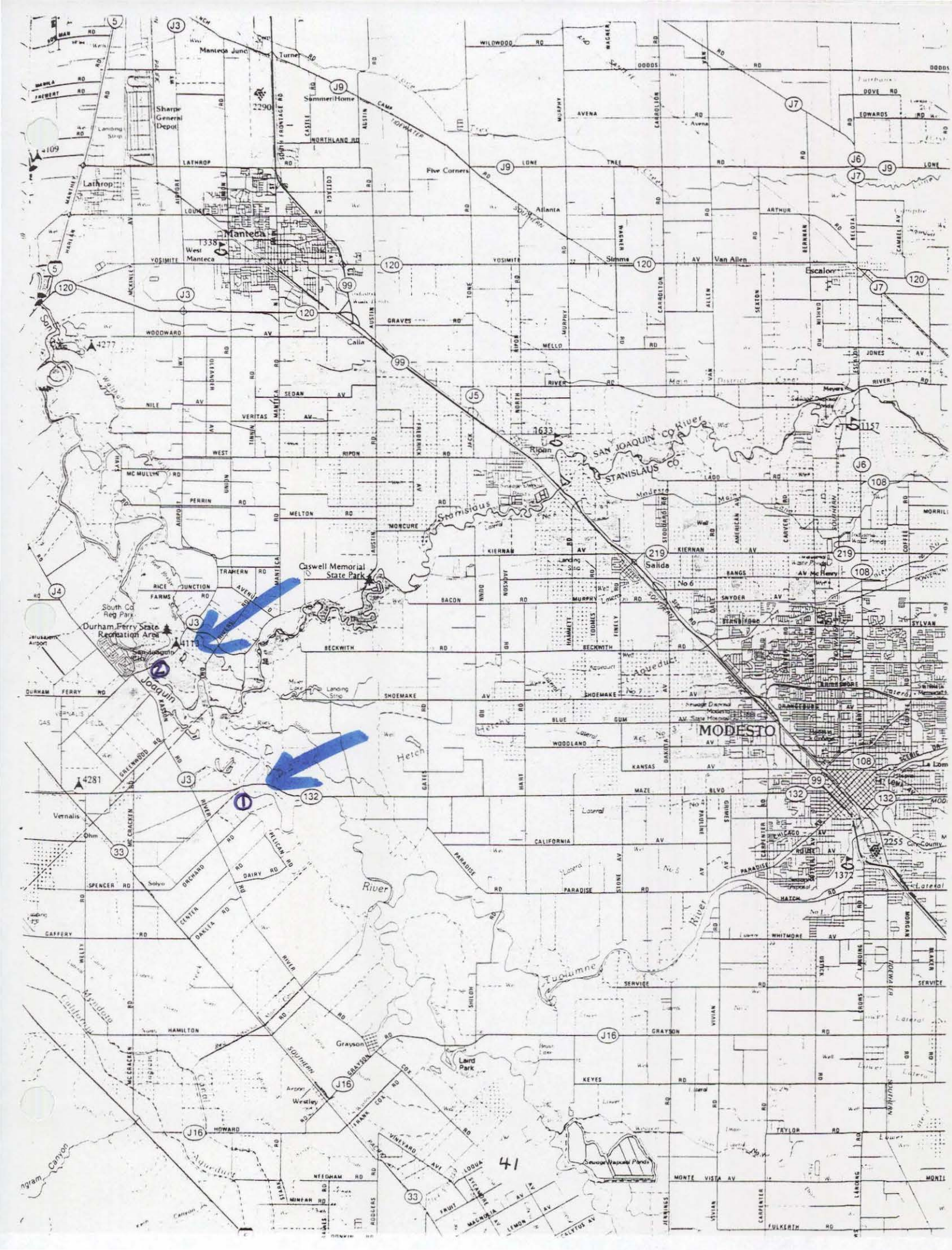
Graph 1



SULFUR VS. SELENIUM

Graph 2

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Van Allen
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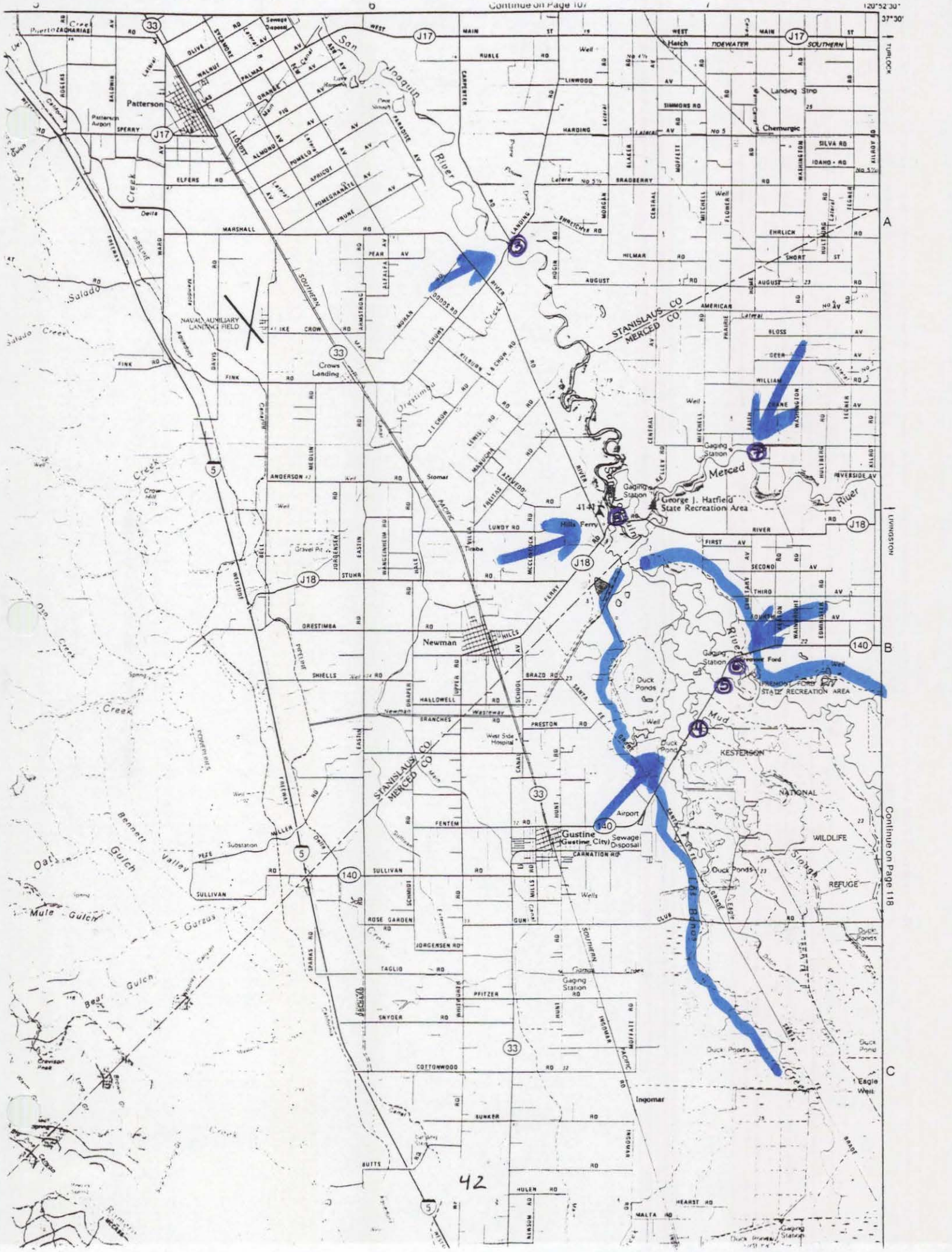
Calla
Ripon
SAN JOAQUIN CO.
STANISLAUS CO.
Caswell Memorial State Park
Durham Ferry State Recreation Area
South Co Reg Park
Salida
MODESTO
Vernalis
Grayson
Westley
Laird Park
Tuolumne River
Stanislaus River
San Joaquin River
Sewage Disposal Ponds
41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Patterson
Newman
Gustine
Crows Landing
Hills Ferry
George J. Hatfield State Recreation Area
Merced River
San Joaquin River
Mud Slough
Salado Creek
Orestimba Creek
Del Puerto Creek
Bear Creed
Oak Gulch
Bennett Valley
Mule Gulch
Gurzus Gulch
Eagle Well
Ingomar
Kesterson National Wildlife Refuge
Stanislaus Co
Merced Co
Turlock
Livingston
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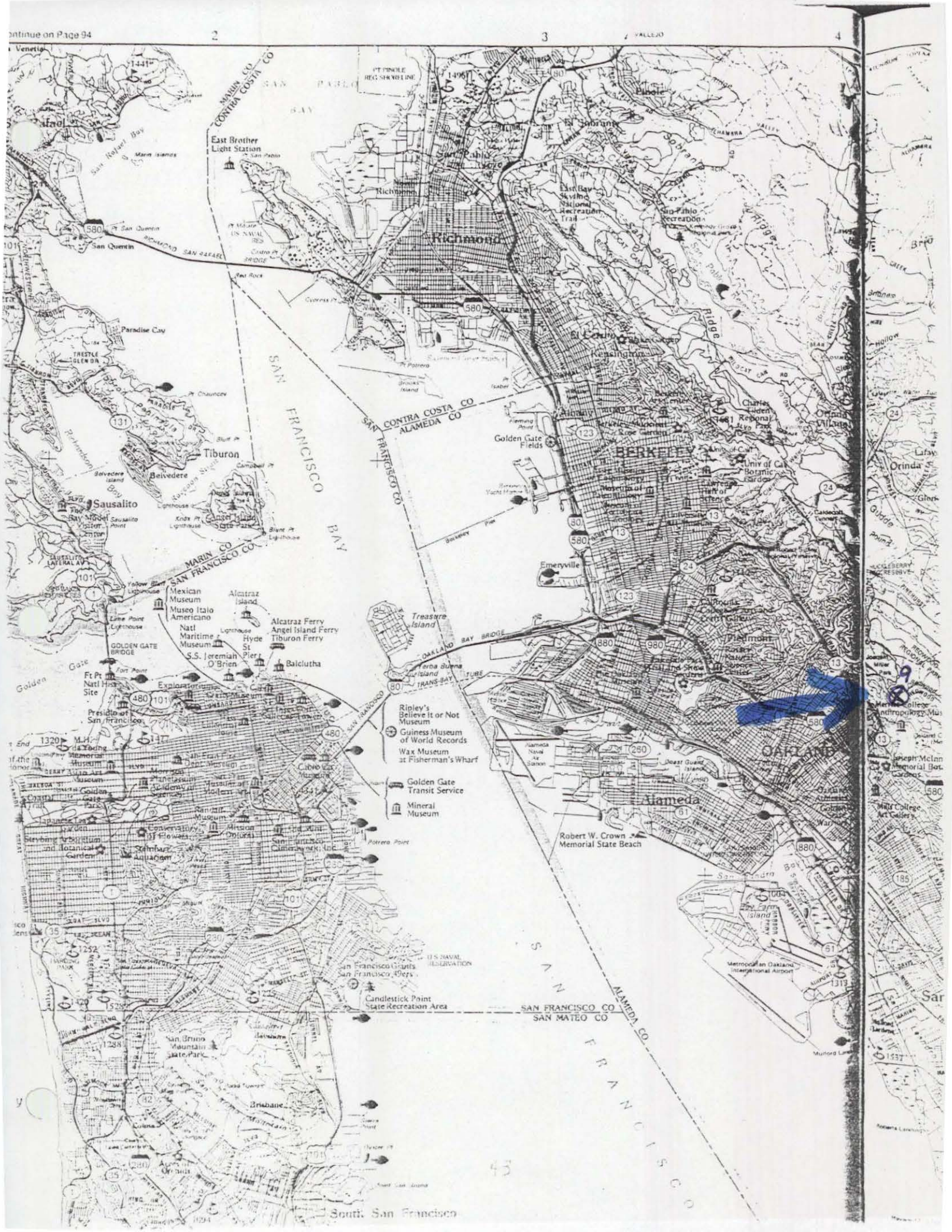

SECTION VI. CONCLUSIONS

The Kesterson National Wildlife Refuge is evidence of how manipulation of the hydrologic cycle, like irrigation and rerouting drainage, can cause water-quality problems if naturally occurring toxic substances are mobilized and concentrated. Sulfur and tellurium which could also be associated with the toxic effects in different environmental systems that results from high selenium levels. Compared to other rivers in the United States and throughout the world, the San Joaquin River has had among the highest concentrations of total selenium [7] and still does. The San Luis Drain, if completed, is to terminate into the Sacramento-San Joaquin Delta, where it will eventually drain into the San Francisco Bay. The San Francisco Bay is upstream spawning grounds for salmon, steelhead, sturgeon, striped bass and shad, and is crucial as a nursery to crabs and shrimp. The selenium will no doubt have an impact on these species. The policy of using drainage water for supply to depleted marshes has already been implemented not only in California but throughout the semiarid West. The threat of selenium accumulation is imminent. Selenium has warranted serious consideration as a contaminant, as serious as others like cadmium, lead, and mercury. There is no doubt that what occurred at the Kesterson NWR is occurring in many more areas.

At twenty-three sites (in 9 western states) surveyed for high concentrations of selenium, seven-Az, Ca, Mt, Nv, NM, SD, and one not named, contained greater than 600 ppb selenium [15].

In Columbia, South America, there have been cases with children being born with severe deformities due to selenium toxicity. The threat is becoming worldwide.

Because of its propensity to bioaccumulate, to move from sediments to biota, and to cause severe adverse reproductive effects as well as mortality, selenium should be recognized as a contaminant with the potential to markedly affect fish, wildlife, livestock, and human populations. And the threat of associated elements like sulfur and tellurium could also have an impact in these contaminated sites as well.

More research is needed to determine whether there is a strong correlation between the selenium and thus sulfur contamination of environmental systems. Because most of the selenium research done has not included the analysis of sulfur and tellurium, not much is known about the relationships between these elements as far as potential side contaminants. But because they are similar in their chemistry and toxicities, an assumption can be make that they are intertwined and their relationship could be deadly to some environmental systems. Both selenium and sulfur are vital to life. Therefore, they are dispersed wherever life exists and necessary for that life. However, once there is too much for the organisms to handle, contamination and toxic effects are bound to occur. Trace metal contaminants have been extensively studied by themselves, however there needs to be an awareness of all the components that surround those elements. The interaction of the biosphere and

the biogeochemical cycling of trace elements could further resolve the problems of agricultural drainage, mining effluents and all the common contamination constituents.

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